

~~PROCESS FOR THE PRODUCTION OF AN ELECTROCHROMIC COATING~~  
<sup>TITLE</sup>  
~~Process for the production of an electrochromic coating~~  
<sup>COATING</sup>  
BACKGROUND OF THE INVENTION

~~Field of the Invention~~  
<sup>Specification</sup>  
~~Field of the Invention~~

The invention relates to a process for the production of an

5 electrochromic coating on a substrate by cathode sputtering of a target in a coating atmosphere containing hydrogen ions, as well as to an electrochromic element with at least one such coating.

10 Designated as electrochromic coatings are coatings which are capable of reversibly absorbing (intercalating) and again emitting (decalating) cations, in particular  $H^+$  ions or  $Li^+$  ions, their optical properties generally changing in this process. They consist principally of metal oxides or  
15 mixed metal oxides. Electrochromic materials include anodically and cathodically colourable materials, as well as pure ion-storage materials, whose optical properties depend only slightly or not at all on the amount of the intercalated cations.

20 Description of the Related Art

Electrochromic elements are increasingly gaining interest as so-called "intelligent windows" whose light transmission or other optical properties can be selectively influenced by temporary application of an electrical voltage. Such  
25 electrochromic elements generally consist of substrates, in

particular of transparent glass or plastic, provided on one side with conductive coatings, an electrochromic coating being arranged in each case on the conductive coatings.

The substrates coated in this way are connected to one another by interposing an electrolyte (ion conductor).

By application of a voltage to the conductive coatings, cations located in the electrochromic element, generally  $H^+$  or  $Li^+$  ions, are intercalated into one of the electrochromic coatings (the electrochromic coating in the actual sense of the term), as a result of which its optical properties change in the desired sense. The other electrochromic coating, which usually consists of a different material as the first-mentioned electrochromic coating, frequently acts as an ion storage coating not significantly altering its optical properties which, on application of a voltage of opposite sign, is capable of absorbing the cations now decalated from the other electrochromic coating.

An electrochromic element of this type can be found for example in publications DE 197 06 918 A1, EP 0 683 215 A1, WO 95/31746 A1. As material for the electrochromic coating in the actual sense, which significantly alters its optical properties during intercalation and decalation of cations, tungsten oxide ( $WO_x$ ) has in practice been found

satisfactory, as mixed oxide or interspersed with doping additives. As material for electrochromic coatings which are used as ion storage coatings, mixed oxides, such as cerium-titanium oxide or vanadium-titanium oxide, are known inter alia.

For the production of such electrochromic coatings, a series of different coating processes are known, these including for example CVD or sol-gel processes, as well as physical processes, such as various vacuum metallizing processes, ion plating or cathode sputtering. For large-area electrochromic elements, cathode sputtering is primarily involved for reasons of cost for the production of the individual coatings, and here in particular reactive DC or medium-frequency magnetron cathode sputtering of metal or semi-conductive targets.

Electrochromic coatings are not generally fully functional directly after their production or after assembly of all components to form an electrochromic element. On the contrary, they must be conditioned, which means that the electrochromic coatings or the electrochromic element are cyclically charged and discharged until the desired maximum transmission range is reached. By transmission range is meant the transmission difference between the coloured and

bleached state of the electrochromic coating or of the electrochromic element. Only subsequently is the electrochromic element usable over a long period of time and can be switched between defined initial and final states. If one conditions electrochromic coatings produced according to the state of the art with the aid of a liquid electrolyte, such as propylene carbonate with Li salt dissolved in it and a standard counter-electrode, one will find that during the initial charge/discharge cycle a significant difference occurs between the intercalated and the deintercalated charge. The so-called "blind charge" (unit:  $\text{mC}/\text{cm}^2$ ) consists of positive charge carriers, for example  $\text{H}^+$  ions or  $\text{Li}^+$  ions which remain irreversibly in the electrochromic coating after the initial charge cycle and thus permanently reduce the number of the charge carriers available for the electrochromic element. It has been observed in the process that, with an increasing positive blind charge, the duration of the necessary conditioning of the electrochromic element increases drastically. A lengthy conditioning process however renders production more costly and is thus undesirable. In addition, electrochromic coatings produced according to the state of the art frequently possess insufficient storage capacity or inadequate colouring efficiency (ratio of

transmission range to intercalated charge per unit of area).

A process according to the preamble of claim 1 is known from GB 2 086 601 A. According to this publication, oxygen and hydrogen vapour are added to the coating atmosphere, in order to produce electrochromic hydroxide coatings from metal targets. As a coating process clearly preferable to cathode sputtering with a coating atmosphere containing water vapour, reactive ion plating with the addition of water vapour is employed. The electrochromic coatings produced in this way are used for the production of electrochromic displays where  $H^+$  ions are used as charge carriers. In a large-scale industrial sputtering process, the addition of water vapour to the coating atmosphere can only be controlled with difficulty and leads to significant lack of uniformity in the coating properties and in the distribution of coating thickness.

## SUMMARY OF THE INVENTION

The object of the invention is to provide a process with which electrochromic coatings can be produced by cathode sputtering with at all events less positive or even negative blind charge. With the process, it should in addition be possible to produce electrochromic coatings with higher storage capacity (absorption capacity) for

positively charged ions, in particular  $H^+$  ions or  $Li^+$  ions. The process should be easier to control than cathode sputtering in a coating atmosphere with addition of water vapour.

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To achieve this object, the invention proposes that at least one gaseous hydrocarbon be added to the coating atmosphere. Especially suitable are the saturated hydrocarbons, and preferably methane. This gaseous saturated hydrocarbon is characterized by an especially high proportion of hydrogen to carbon per molecule. It has been found that the desired effects of the addition to the coating atmosphere according to the invention is best achieved if the ratio of hydrogen to carbon in the molecule of the hydrocarbon is high, as with excessive carbon content of the molecule, excessive carbon is incorporated in the coatings, as a result of which the electrochromic properties can deteriorate. In addition, it is possible with a high H:C ratio, to set the overall pressure of the coating atmosphere comparatively low and thus the coating rate relatively high. Other suitable gases are primarily ethane, propane or butane. Of course, a noble gas is also added to the coating atmosphere at all times - this is normally argon - this being required as non-reactive gas for target sputtering.

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Especially with the reactive cathode sputtering of metal or semi-conductive targets specially preferred within the scope of the invention, oxygen is additionally added to the coating atmosphere. The volume ratio of added hydrocarbon to added oxygen is preferably set in the range of 3:1 to 1:3, especially at approximately 1:1. With lower levels of hydrocarbons, the desired effects can no longer be achieved to a sufficient extent, whilst with higher levels of hydrocarbons, the electrochromic properties of the coatings deteriorate or the sputtering process is more difficult to control.

It is especially preferable during cathode sputtering for the volume ratio of argon to oxygen to be in the range of 3:1 to 1:3, in particular at approximately 1:1.

The stated ratios are set by means of corresponding adjustments of the metering valves for the gases in question. A ratio of 1:1 corresponds for example to the same setting of the gas flow rate for both gases.

A sufficiently high coating rate, as well as especially good coating properties, are achieved if one employs an

overall gas pressure of the coating atmosphere of  $0.3 \cdot 10^{-2}$  mbar to  $10^{-1}$  mbar, especially of  $1 \cdot 10^{-2}$  mbar to  $4 \cdot 10^{-2}$  mbar.

5 The process according to the invention is especially suitable for the production of electrochromic coatings with tungsten oxide base, for which then a target of tungsten or tungsten alloy is employed. Another application provides for the use of a target containing molybdenum, titanium, cerium, vanadium and/or zirconium.

10 The process is preferably carried out such that electrochromic coatings with a thickness in the range of 50 nm to 500 nm are obtained. Normally, thinner coatings no longer possess an adequate transmission range or an adequate storage capacity for charge carriers. Thicker coatings provide no significant advantages and can no longer be produced cost-effectively in uniform quality.

20 With electrochromic coatings produced according to the invention, it is possible to produce electrochromic elements with high colouring efficiency (high transmission range per intercalated charge per unit of area). In addition, in some cases, an increased intercalation rate of  $H^+$  ions and  $Li^+$  ions could also be observed in

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electrochromic coatings produced in this way, so that it was possible to produce electrochromic elements with higher operating rate than with conventionally applied electrochromic coatings. Above all, the time required for conditioning the electrochromic element can be significantly reduced by the use of the invention. It was also found that electrochromic coatings produced according to the invention possess higher thermal resistance in comparison with coatings having been produced without addition to the coating atmosphere according to the invention. It is supposed that at least part of these effects is based on incorporation of carbon atoms in the matrix of the electrochromic material. In fact, it was found for coatings produced according to the invention by thermodesorption analysis that they contained carbon in the order of magnitude of some atomic percent. The invention has proved especially satisfactory in the production of electrochromic elements with  $\text{Li}^+$  ions as charge carriers, in particular with a polymer electrolyte according to WO 95/31746 A1.

The invention can be applied to special advantage during reactive DC or medium frequency sputtering of metal or semi-conductive targets in a coating atmosphere containing argon, oxygen and hydrocarbon(s). Basically however, it

can also be used in HF sputtering of oxidic targets, where of course the oxygen content of the coating atmosphere will normally be lower than is the case with reactive cathode sputtering. Electrochromic coatings produced according to the invention are used to special advantage for production of hermetically sealed electrochromic elements, where the number of charge carriers available for charge transfer is limited. Here, the invention is not confined to electrochromic elements with  $\text{Li}^+$  ions as charge carriers. On the contrary, it is also possible to use  $\text{H}^+$  ions or other positively charged ions.

The invention is explained below with the aid of examples.

## BRIEF DESCRIPTION OF THE DRAWING

The single Figure illustrates in schematic form an electrochromic element with an electrochromic coating

produced according to the invention. ~~The electrochromic~~

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electrochromic element consists of a first glass pane 10 and a second glass pane 12, both of which are essentially flat and have dimensions of for example approximately  $40 \cdot 80 \text{ cm}^2$ . The first glass pane 10 bears on its surface facing downwards in the drawing a first conductive layer 14, this being for example an indium-tin oxide (ITO) coating with a thickness of 300 nm. Onto the first conductive layer 14 is applied an electrochromic coating 16 of  $\text{WO}_x$  by a process according

to the invention. The second glass pane 12 bears on its side facing towards the first glass pane 10 a second conducting layer 18, which for example also consists of indium-tin oxide, with a thickness of 300 nm. Adjacent to the second conductive layer 18, on the side opposite to the second glass pane 12 is an ion storage coating 20 of  $\text{Ce}_x\text{Ti}_y\text{O}_z$  with a thickness of 280 nm, which has preferably been produced by a process according to the invention. The two glass panes 10, 12 provided with coatings described above are bonded to one another in the manner of a laminated pane by an ion conduction layer 22, which in the case of the example illustrated has a thickness of 1 mm and consists of a plastic matrix with embedded salts (polymer electrolyte). An edge seal 24 seals the ion conduction layer 22 towards the outside of the element; through it are also led out in customary fashion the contacts 26, 28 which are connected to the electrode layers 14, 18.

The examples below illustrate with the aid of the coating of specimen glass panes according to a known process and according to processes according to the present invention how blind charge and conditioning time are reduced in the presence of hydrocarbons in the coating atmosphere.

Examples 1 - 4

Glass panes measuring  $10 \cdot 10 \text{ cm}^2$  with a thickness of 2 mm provided with indium-tin oxide (ITO) as conductive layer with a surface resistance of  $10 \Omega$  were coated in a DC magnetron cathode sputtering system with  $\text{WO}_x$  corresponding to Column 2 of Table 1. The composition of the coating atmosphere in each case is stated in Columns 3 - 7. The blind charge has been determined subsequent to coating production by the coated pane being immersed in a liquid electrolyte (polypropylene carbonate with  $\text{Li}^+$  salt) and being subjected to a charge/discharge cycle, where the blind charge is determined as difference of the charge per unit area which had flowed in each case. The conditioning time was determined on complete electrochromic elements with the structure: glass / ITO conductive layer /  $\text{WO}_x$  electrode / polymer electrolyte / Ce-Ti oxide counter-electrode / ITO conductive layer / glass.

Table 1

Ex. No.	Thickness [nm]	Relative Volume Parts Ar	Relative Volume Parts O <sub>2</sub>	Relative Volume Parts HC	HC	Total pressure [10 <sup>-2</sup> mbar]	Blind charge [mC/cm <sup>2</sup> ]	Cond. time [h]
1	255	4	3	--	--	1.4	10.7	60
2	260	2	2	1	methane	2.5	3.2	20
3	255	2	2	2	methane	3.3	-0.3	1
4	270	2	2	2	ethane	3.8	0.8	4

It becomes clearly recognizable that the blind charge, and thus the conditioning time, is significantly reduced due to the addition of a hydrocarbon gas according to the invention. The coating process took place in comparably stable fashion. No undesirable contamination of the coating apparatus was observed.

Additional trials not described here evidenced a reduced blind charge and overall improved coating properties also with ion storage coatings such as cerium-titanium oxide or titanium-vanadium oxide.

Of course, the invention is applicable to electrochromic elements other than those described as examples. Thus, materials other than ITO, for example SnO<sub>2</sub> doped with fluorine or antimony, can be employed for the conductive layers. It is also possible to use other electrolytes in

place of the preferably employed polymer electrolytes according to WO 95/31746 A1. The advantages of the invention are of course to be found above all with hermetically sealed electrochromic elements with a limited quantity of charge carriers. It can also however be employed to advantage in the case of electrochromic elements which are saturated or even supersaturated with charge carriers prior to assembly.

The features disclosed in the foregoing description, in the claims and/or in the accompanying drawing may, both separately and in any combination thereof, be relevant for realizing the invention.